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R. E. DOOLITTLE, Acting Chief of Bureau.

THE DETERMINATION OF TARTARIC ACID.

By P. B. DUNBAR, *Assistant Chemist, Division of Foods.*

INTRODUCTION.

The usual method for the determination of tartaric acid is one which depends upon the precipitation and titration of insoluble acid potassium tartrate. This method was first described by Berthelot and Fleurieu [1] in 1865, and has since undergone frequent modifications at the hands of various workers. The method proposed by Halenke and Möslinger [2] is perhaps the most used of these modifications. Although capable of considerable accuracy under proper conditions, it is open to the objections that the reaction between the acid and the precipitate is never complete and the results are often influenced to a great degree by other substances present in the solution.

The method of Chapman and Whitteridge,[3] in which the acid is precipitated as bismuth tartrate and subsequently oxidized with potassium permanganate in acid solution, is not applicable in the presence of citric, malic, and oxalic acids. J. von Ferentzy [4] has described a method for the determination of tartaric acid in the presence of malic and succinic acids which is based on the insolubility of basic magnesium tartrate in 50 per cent alcohol. According to L. Gowing-Scopes,[5] who has studied the method, it is capable of a high degree of accuracy. E. B. and F. B. Kenrick [6] have developed a polariscopic method for the determination of tartaric acid and tartrates depending on the rotation of the acid in the presence of an excess of ammonia, while Richardson and Gregory [7] have described a similar method in which advantage is taken of the increase in the optical activity of tartaric acid on treatment with ammonium molybdate. One of the most recent methods is that of

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[1] Berthelot's Chimie Vegetale et Agricole, 1899, **4**: 423.
[2] Zts. Anal. Chem., 1895, **34**: 263; U. S. Dept. Agr., Bureau of Chemistry, Bul. 107, Rev., p. 86.
[3] Analyst, 1907, **32**: 163.
[4] Chem. Ztg., 1907, **31**: 1118.
[5] Analyst, 1908, **33**: 315.
[6] J. Amer. Chem. Soc., 1902, **24**: 928.
[7] J. Soc. Chem. Ind., 1903, **22**: 405.

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Kling[1] in which tartaric acid is precipitated in the form of calcium racemate. Warcollier,[2] who has applied the method to a number of fruit juices, reports very accurate results.

The fact that under certain conditions uranium salts produce a marked increase in the specific rotation of the dicarboxylic-oxyacids has recently been made the basis of a quantitative method for the determination of l-malic acid, first by Yoder[3] and later by Dunbar and Bacon.[4]

As the specific rotation of d-tartaric acid is increased by treatment with uranium salts,[5] the presence of this acid interferes with the determination of malic acid by the optical method. The present investigation was undertaken for the purpose of devising a method for the determination of tartaric acid which might also be applied to the determination of both malic and tartaric acids in the same solution. The method finally devised for the determination of tartaric acid, while not capable of the accuracy of the malic acid method, is nevertheless, believed to be of sufficient value to warrant presentation. It will be given in this circular, while the procedure employed for the determination of both acids in the same solution is described in Circular 105 of this bureau.

The possibility of determining d-tartaric acid by means of the increase in rotation produced on treatment with uranium salts has been pointed out by Yoder,[6] who has presented some brief notes on the subject based on his experiments with malic acid. The procedure suggested by Yoder, however, was not found to be capable of successful application, and a search was therefore made for the conditions under which the effect of uranyl acetate on the rotation of solutions of tartaric acid is proportional to the amount of tartaric acid present within a reasonable range of concentration.

EXPERIMENTAL WORK.

If treatment with uranyl acetate produces an increased rotation in tartaric-acid solutions proportional to their concentration, it should be possible to determine the amount of the acid present in a solution containing other optically active substances not affected by the uranium salt by simply polarizing the solution after treatment with the reagent and multiplying the difference between this reading and that of the solution which has been freed from tartaric acid by a factor determined experimentally.

In the earliest experiments the attempt was made to apply the same method which is used in the determination of malic acid.[7]

[1] Bull. assoc. chim. sucrerie, 1910, **28**: 893; Compt. rend., 1910, **150**: 616; Ann. fals., 1910, **3**: 239.

[2] Ann. fals., 1911, **4**: 485.

[3] J. Ind. Eng. Chem., 1911, **3**: 563.

[4] U. S. Dept. Agr., Bureau of Chemistry, Cir. 76; J. Ind. Eng. Chem., 1911, **3**: 826.

[5] Walden, Ber. d chem. Ges., 1897, **30** (3): 2889.

[6] J. Ind. Chem., 1911, **3**: 573.

[7] Dunbar and Bacon, U. S. Dept. Agr., Bureau of Chemistry Cir. 76; J. Ind. Eng. Chem., 1911, **3**: 826.

Solutions of tartaric acid, both before and after neutralization with sodium hydroxid, were treated with powdered uranyl acetate and allowed to stand with frequent shaking. Portions of the solutions were filtered and polarized at intervals. It was found to be impossible under these conditions to obtain solutions of constant rotations. In the more dilute solutions, containing less than 0.5 gram of tartaric acid per 100 cc, the first readings were made 1 hour after the addition of uranyl acetate and these were the highest obtained. Hourly readings made thereafter showed a slow drop in rotation, an approximately constant reading being obtained only after from 1 to 3 days. In the more concentrated solutions of tartaric acid, the time required to attain a maximum rotation increased with the concentration and was also influenced to a marked degree by the frequency with which the mixture was shaken. In a solution containing 2 grams of tartaric acid per 100 cc, for example, a maximum rotation, +49.0° V., was attained in 6½ hours, while in the same series of experiments the solution containing 3 grams of acid per 100 cc required 48 hours to reach a maximum, +70.3° V. After reaching a maximum a slow fall in rotation was observed in most cases. Several series of tartaric-acid solutions, ranging in concentration from 0.2 to 4.0 grams of acid per 100 cc, were treated in the manner described, with similar results.

It was then suggested that the variations in rotation might be due to the action on the uranium-tartaric complex of acetic acid formed by hydrolysis of uranyl acetate. Five grams of sodium acetate were therefore dissolved in the neutralized solutions before diluting to the final concentration. Under this treatment the time required to reach a maximum was not shortened, but the tendency of the rotation to decrease after reaching a maximum appeared to be somewhat less marked. It was also noticed that the solubility of uranyl acetate in the solutions was markedly decreased.

Various attempts were then made to drive the rotation to a maximum in the course of a few hours. Ammonium uranate was substituted for uranyl acetate without result. When solutions of tartaric acid and sodium acetate were treated with uranyl acetate and heated on a steam bath with a reflux condenser, maximum rotations which remained fairly constant were obtained in from 1 to 2 hours, but in the presence of sugars sufficient caramelization often occurred to ruin the determination. Agitation of the solutions with uranyl acetate with a mechanical shaking device was finally found to produce a maximum change in rotation in a few hours.

Solutions containing the same amount of tartaric acid give a somewhat lower rotation when neutralized before treatment with uranyl acetate than when treated with the reagent without neutralization. Free mineral acids prevent the formation of the uranyl-tartaric com-

plex, and acetic acid appears to have a disturbing influence on the rotation. As these acids may be present in a solution under examination, it is always necessary to neutralize the solution before treatment with uranyl acetate. It is desirable to use an acid solution because a larger change in rotation may be obtained. When the neutralized solution is acidified with citric acid, the rotation of the solution is not disturbed.

The most successful method of procedure is as follows:

Render a measured volume of the tartaric-acid solution slightly alkaline to litmus paper with sodium hydroxid, dissolve 5 grams of sodium acetate in the solution, reacidify with a strong citric-acid solution, adding a slight excess of the acid, and dilute to 100 cc. Treat this solution with powdered uranyl acetate and agitate with a mechanical shaker for 3 hours. Enough uranyl acetate must be added so that a small amount remains undissolved at the end of the period of shaking. The optical rotation of solutions containing between 0.2 and 3 grams of tartaric acid per 100 cc when treated in this manner is closely proportional to the amount of tartaric acid present in the solution.

DETERMINATION OF THE FACTOR.

A large number of experiments were made to determine the factor to be used in calculating the amount of tartaric acid from the polarization of the solution after treatment with uranyl acetate. Solutions containing known amounts of pure tartaric acid were treated in the manner described above and polarized in 200-mm tubes, using white light. The factor was obtained by dividing the weight in grams per 100 cc of tartaric acid present by the rotation in degrees Ventzke. The results are shown in Table 1. The average factor is 0.051, and this has been adopted for use in all calculations.

TABLE 1.—*Determination of the factor.*

Tartaric acid present (grams per 100 cc).	Polarization in 200-mm tube.	Factor calculated.	Tartaric acid found using factor 0.051.	Tartaric acid present (grams per 100 cc).	Polarization in 200-mm tube.	Factor calculated.	Tartaric acid found using factor 0.051.
	°*V*.				°*V*.		
2.50	+49.6	0.050	2.53	[1] 0.99	+19.3	0.051	0.98
2.00	+37.9	.053	1.93	[1] .99	+18.6	.053	.95
2.00	+38.8	.052	1.98	.50	+ 9.9	.050	.50
2.00	+39.0	.051	2.00	[1] .50	+10.2	.049	.52
1.75	+35.5	.049	1.81	[1] .50	+ 9.5	.053	.48
1.50	+30.8	.049	1.57	.40	+ 8.0	.050	.41
1.50	+30.0	.050	1.53	.30	+ 5.7	.053	.29
[1] 1.49	+29.4	.051	1.50	.25	+ 4.6	.054	.23
[1] 1.49	+28.7	.052	1.46	.20	+ 3.9	.051	.20
1.00	+21.1	.047	1.08				
1.00	+20.5	.049	1.05	Average factor....		.051	

[1] Determinations by Dr. J. M. Johnson.

As has been stated, the concentration of tartaric acid is practically proportional to the rotation of the uranium-tartaric solution in solutions containing between 0.2 and 3.0 grams of the acid per 100 cc, the ratio being 0.051. Beyond this point the ratio gradually increases. This is probably due partly to a normal decrease in specific rotation with rise in concentration and partly to the diluting effect of the solution of uranyl acetate. A 4 per cent solution of tartaric acid is increased approximately 4 per cent in volume after treatment with uranyl acetate. The increased rotation of the uranium-tartaric solution as compared with the rotation of the straight tartaric-acid solution is shown graphically by the curves in figure 1. *A* represents the rise in rotation with concentration of solutions of pure tartaric acid, while *B* shows the increase in rotations of the same solutions after treatment with uranyl acetate.

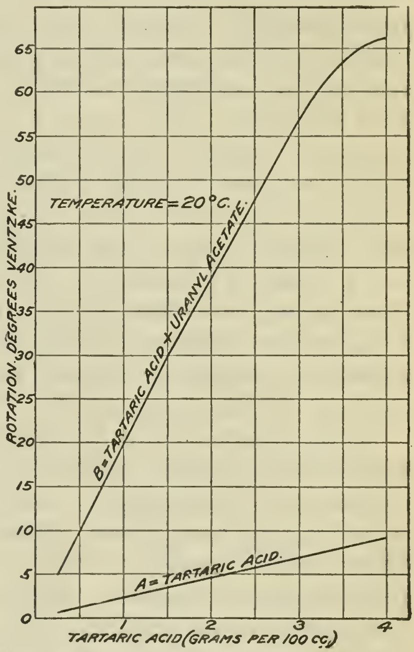

FIG. 1.—Comparison of uranium-tartaric and straight tartaric acid solutions.

REMOVAL OF TARTARIC ACID.

Walden[1] reports $(\alpha)_D$ for a solution containing 0.75 gram of tartaric acid per 100 cc as approximately +14.7 circular degrees as compared with +303° for the uranium complex. It is evident that when solutions are under examination which contain other optically active substances in addition to tartaric acid, the latter will have a noticeable effect on the original rotation of the solution. It is, therefore, necessary to remove the tartaric acid from the solution in order to determine the rotation due to other optically active substances present. Dry powdered normal lead acetate is quite satisfactory for this purpose.

Uranyl acetate produces a slight effect on the rotation of sugars.[2] In solutions containing a sman amount of tartaric acid (under 0.5 per cent) and a rather large amount of sugars (over 10 per cent), it is necessary, therefore, to treat the original solution with uranyl acetate after precipitating the tartaric acid and removing the excess of lead with anhydrous sodium sulphate.

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[1] Ber. d. chem. Ges., 1897, 30: 2890.

[2] U. S. Dept. Agr., Bureau of Chemistry Cir. 76, p. 5; J. Ind. Eng. Chem., 1911, 3: 826.

The solubility of lead tartrate in water at 25° C. is 0.0108 gram per 100 cc.[1] Consequently, the amount of tartaric acid remaining in the solution after precipitation with lead acetate is not sufficient to cause any noticeable increase in the rotation of the solution when uranyl acetate is added.

DETAILS OF THE METHOD.

(1) Measure 85 cc of the solution under examination into a 100 cc graduated flask, render the solution slightly alkaline to litmus paper with sodium hydroxid, add 5 grams of sodium acetate and shake until dissolved. Reacidify the solution to litmus paper with a strong solution of citric acid, adding a slight excess of the acid, cool to room temperature, and dilute to 100 cc. Treat about 30 cc of this solution with powdered uranyl acetate, transfer to a suitable container, and shake for 3 hours with a mechanical shaker. Add enough uranyl acetate so that a small amount remains undissolved after 3 hours shaking; from 2 to 3 grams are usually sufficient. If the uranium salt dissolves, more must be added. Filter through a folded filter and polarize, if possible, in a 200 mm tube. After polarizing, agitate the solution for an hour longer with uranyl acetate and again polarize to determine whether a maximum rotation has been obtained. Calculate the reading in degrees Ventzke to the basis of the original solution and designate as (1).

(2) Treat about 50 cc of the original solution with dry powdered normal lead acetate until no further precipitation results; avoid excess of the precipitant. A centrifuge can be used to advantage in settling the precipitate. Filter through a folded filter and test the filtrate with a small crystal of lead acetate to determine whether precipitation is complete. Remove the excess of lead with powdered anhydrous sodium sulphate, filter until clear, and polarize in a 200 mm tube. Designate this reading as (2). If the solution is supposed to contain less than 0.5 per cent of tartaric acid and more than 10 per cent of sugar, treat the tartaric acid free solution with powdered uranyl acetate and shake at intervals for 1 hour. Filter and polarize. If the reading so obtained is less than (2), it should be used instead of (2) in the final calculation.

(3) Polarize at room temperature with white light, taking care that all solutions are polarized at the same temperature. Make at least six readings on each solution and take the average of these. Calculate all readings to the basis of a 200 mm tube. Multiply the algebraic difference in degrees Ventzke between readings (1) and (2) by the factor 0.051. The result will equal the weight of total tartaric acid in grams in 100 cc of the original solution.

[1] Partheil and Hübner, Arch. Pharm., 1903, 241: 412; Chem. Centralbl. 1903, 74 (2): 1026.

NOTES ON THE METHOD.

In this work a standard, Lippich type, triple-field saccharimeter was used, the light being furnished by an electric stereopticon bulb placed behind a ground-glass plate.

The most favorable concentration of tartaric acid for the determination is between 0.5 and 2.0 gram per 100 cc. Solutions containing as low as 0.2 gram per 100 cc may be determined with accuracy, however, when the color of the solution is not such as to make readings uncertain.[1]

After reaching a maximum, the rotation of the uranium-tartaric solution remains constant and solutions may be kept overnight before polarizing. They must be kept in a dark place, however, as they are darkened by exposure to daylight.

It is sometimes advantageous in solutions containing large amounts of pectin bodies to precipitate the latter with two or three volumes of alcohol, wash the precipitate with 95 per cent alcohol and concentrate the filtrate to the original volume, following the procedure for the determination of malic acid in fruit juices described by Pratt.[2]

In very clear solutions containing large amounts of tartaric acid, difficulty is sometimes experienced in polarizing owing to the blue color developed in one segment of the field. Under these circumstances it is advisable to dilute the solution.

A few experiments were made to determine the effect of phosphates, iron, and aluminum on the results. In the concentrations studied, the presence of iron or phosphates does not appear to affect the accuracy of the results. A solution containing 0.50 gram of tartaric acid and 1 gram of di-sodium phosphate in 100 cc yielded 0.49 gram of tartaric acid while another containing the same amount of tartaric acid and 1 gram of ferrous sulphate yielded 0.46 gram. Only 0.36 gram of tartaric acid was recovered from a solution containing 0.50 gram of the acid and 1 gram of potassium alum in 100 cc.

DISCUSSION OF RESULTS.

The results are tabulated in Tables 2 and 3. Table 2 contains the record of determinations on solutions of tartaric acid with various sugars. The percentages of sugar given in column 2 are only approximate. This explains the variations in rotation between solutions which are designated as having the same concentration of sugar. The determinations on fruit juices recorded in Table 3 were made on solutions in which the amounts of added tartaric acid were unknown

[1] In Bureau of Chemistry Cir. 76, p. 8, Determination of Malic Acid, the use of bromin as a bleaching agent for dark-colored solutions was suggested. Discordant results recently obtained, however, indicate that bromin affects the rotation of the uranium complex. A study of the best methods of bleaching dark-colored solutions before polarization is now in progress.

[2] U. S. Dept. Agr., Bureau of Chemistry Cir. 87.

to the analyst. It will be noted that the results on blackberry juice and in the lower concentrations on raspberry juice vary most widely from the theoretical. This is due to the fact that the color of these solutions is so intense that a considerable error is likely to be introduced in making the polarizations.

Numerous attempts were made to obviate this difficulty in dark-colored solutions by precipitating the tartaric acid with lead acetate in the presence of three or four volumes of alcohol, decomposing the precipitate with sulphuric acid or hydrogen sulphid, concentrating the resulting filtrate and determining the tartaric acid in the solution so obtained. The solutions finally obtained, however, were almost as highly colored as the original samples and the results were irregular and unsatisfactory.

TABLE 2.—*Determination of tartaric acid in sugar solutions.*[1]

Kind of sugar.	Amount of sugar present (approximate).	Tartaric acid added (grams per 100 cc).	Polarization in 200 mm tubes.[2] After treatment with uranyl acetate.	Polarization in 200 mm tubes.[2] Solution freed from tartaric acid.	Difference between readings.	Tartaric acid found (grams per 100 cc).
	Per cent.		°*V.*	°*V.*	°*V.*	
Sucrose	25.0	0.50	+102.8	+ 93.5	9.3	0.47
Do	25.0	.49	+102.4	+ 93.2	9.2	.47
Do	25.0	.25	+ 98.3	+ 94.5	3.8	.19
Do	12.5	.25	+ 52.0	+ 47.3	4.7	.24
Dextrose	25.0	.50	+ 86.2	+ 76.5	9.7	.49
Do	25.0	.49	+ 84.7	+ 74.1	10.6	.54
Do	25.0	.49	+ 86.5	+ 76.1	10.4	.53
Do	25.0	.25	+ 81.2	+ 77.3	3.9	.20
Do	12.5	.25	+ 42.8	+ 38.2	4.5	.23
Levulose	22.0	.50	− 99.5	−109.0	9.5	.48
Do	25.0	.49	−123.8	−135.3	11.5	.59
Do	25.0	.25	−115.8	−120.8	5.0	.26
Do	12.5	.25	− 54.7	− 59.2	4.5	.23
Invert	25.0	.98	− 5.4	− 24.6	19.2	.98
Do	12.5	.98	+ 10.2	− 12.7	22.9	1.17
Do	25.0	.50	− 11.3	− 17.2	5.9	.30
Do	25.0	.50	− 8.9	− 18.7	9.8	.50
Do	25.0	.50	− 21.0	− 29.6	8.6	.44
Do	10.0	.50	− .9	− 11.4	10.5	.54
Do	25.0	.49	− 10.6	− 20.0	9.4	.48
Do	25.0	.49	− 12.6	− 22.2	9.6	.49
Do	12.5	.49	.0	− 10.8	1.1	.55
Do	25.0	.25	− 15.5	− 19.2	3.7	.19
Do	25.0	.25	− 24.9	− 29.1	4.2	.21
Do	25.0	.25	− 16.6	− 21.3	4.7	.24
Do	12.5	.25	− 4.0	− 9.0	5.0	.26
Do	10.0	.25	− 6.0	− 11.0	5.0	.26
Do	7.0	.25	− 1.2	− 6.7	5.5	.28
Do	25.0	.13	− 26.6	− 29.1	2.5	.13
Do	10.0	.13	− 8.7	− 10.4	1.7	.09

[1] Most of the determinations were made by J. M. Johnson, whose assistance is gratefully acknowledged.
[2] Calculated to original concentration.

TABLE 3.—*Determination of added tartaric acid in fruit juices.*

Fruit juice.	Tartaric acid added (grams per 100 cc).	Polarization in 200 mm tubes.[1] After treatment with uranyl acetate.	Polarization in 200 mm tubes.[1] Solution freed from tartaric acid.	Difference between readings.	Tartaric acid found (grams per 100 cc)
		°V.	°V.	°V.	
Strawberry	0.75	+ 8.3	− 6.2	14.5	0.74
Do	.63	+ 5.2	− 6.1	11.3	.57
Do	.60	+ 4.1	− 6.2	10.3	.53
Do	.50	+ 3.1	− 6.4	9.5	.48
Do	.50	+ 4.5	− 6.6	11.1	.47
Do	.38	+ 1.1	− 6.3	7.4	.38
Do	.35	− 1.0	− 6.8	5.8	.30
Do	.20	− 6.3	−10.3	4.0	.20
Raspberry	1.00	+14.5	− 5.0	19.5	.99
Do	.75	+ 6.3	− 8.4	14.7	.75
Do	.70	+ 5.3	−10.1	15.4	.79
Do	.50	+ 2.1	− 8.0	10.1	.52
Do	.40	− 1.1	−10.4	9.3	.47
Do	.25	− 3.1	− 9.6	6.5	.33
Do	.13	− 5.0	− 6.6	1.6	.08
Blackberry	.60	− .4	− 9.0	8.6	.44
Do	.51	+ 2.8	− 8.0	10.8	.55
Do	.50	+ 2 2	−10.6	12.8	.65
Do	.28	− 2.8	− 9.2	6.4	.33
Do	.13	− 6.0	− 9.6	3.6	.18
Do	.10	−11.9	−12.9	1.0	.05

[1] Calculated to concentration of the original solution.

SUMMARY.

When a solution of tartaric acid or tartrates containing between 0.2 and 3.0 grams of total tartaric acid per 100 cc is treated under definite conditions with uranyl acetate, its optical rotation is markedly increased and is proportional to the amount of tartaric acid present in the solution.

Under these conditions, each gram of tartaric acid present in 100 cc of the solution produces a rotation of +19.6°V., the ratio of tartaric acid concentration to rotation being 0.051.

Malic acid is the only other common acid which is affected in this way by uranyl acetate. Hence, in the absence of malic acid, tartaric acid may be determined quantitatively by treating its solution, properly prepared, with uranyl acetate, polarizing and multiplying the reading by the factor 0.051.

In the presence of other optically active substances, a portion of the solution must be freed from tartaric acid by precipitation with lead acetate and polarized separately. The algebraic difference between this reading and that obtained on the solution which has been treated with uranyl acetate will give the polarization due to the uranyl tartaric complex.

The most favorable limits of concentration are between 0.5 and 2.0 grams of tartaric acid per 100 cc. A determination may easily be made in 4 hours, during 3 of which no treatment except shaking is required.

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